Durability of High Level Waste and Spent Fuel Disposal Containers - an overview of the combined effect of chemical and mechanical degradation mechanisms

Appendix B.2 - Corrosion of Carbon Steel

Fraser King
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Preface

This report is part of a series of six technical documents describing the expected corrosion behaviour of candidate materials for the manufacture of disposal containers for High Level Waste (HLW) and spent fuel in relevant conditions. Currently, candidate materials include: copper, carbon steel, cast iron, titanium, stainless steel and nickel alloys.

The specialist information contained in this document has been compiled in the format of a technical appendix (as opposed to a standard report), since it intends to provide technical input to studies accessible to a broader technical audience rather than form the basis of a stand-alone study. The documents were initially completed in 2010 (King and Watson, QRS-1384J-1, 2010) and were later on updated on the basis of additional information that become available subsequently (with the exception of that on cast iron, which is new, and that on lead which, was not updated).
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Table B2.2: Summary of ‘critical’ (in bold font) and ‘marginal’ (in normal font) conditions for carbon steel HLW/SF containers as a result of operational factors ................................................................. 34
B2.1 Introduction

Carbon (or mild) steel has been proposed as a container material for the disposal of HLW/SF in a number of countries. Carbon steel is the reference container material in Switzerland (Johnson and King 2003, 2008), France (Féron et al. 2009), Belgium (with a cementitious buffer) (Kursten and Druyts 2008, Kursten et al. 2011), and Japan (JNC 2000) and is an alternative material for sedimentary host rock in Canada (King 2007). At various times, carbon steel has also been considered in the German (Kursten et al. 2004), the UK HLW/SF (Marsh and Taylor 1988) and ILW (Smart et al. 2004) disposal concepts, and in the US Yucca Mountain Project (Brossia and Cragnolino 2000).

Carbon steel has a number of obvious benefits as a container material, including: (i) good combination of strength and ductility, (ii) generally good corrosion properties in the expected disposal environment, (iii) extensive experience with fabricating and sealing large cylindrical objects, and (iv) the relative abundance and low cost of the material.

Containers fabricated from carbon steel have historically been associated with disposal facilities in sedimentary host rocks (e.g., Opalinus clay, Boom clay, Callovo-Oxfordian clay in France, and limestone or shales in Canada). This association is a result of the perception that carbon steel would only provide relatively short-term containment (of the order of 1000 years), which may be all that is necessary in sedimentary formations of low hydraulic conductivity. However, as more information has become available about the expected corrosion behaviour of carbon steel containers, the predicted lifetimes have increased, to the point at which carbon steel could also be considered as a suitable material for host rock formations of higher hydraulic conductivity.

Useful summaries of the corrosion behaviour of carbon steel containers are provided by Kursten et al. (2004), Andra (2001), Féron et al. (2009), Johnson and King (2003), King (2007), Smart (2009), and Smart et al. (2004).
B2.2 Carbon steels

Carbon steel is a term used for alloys of iron and carbon with a C content of <2 wt.%, typically containing Mn (<1.65 wt.%), Si (<0.60 wt.%), and Cu (<0.60 wt.%) and with minor amounts of other alloying elements such as Cr, Ni, Mo, Ni, W, V, and Zr (ASM 1987). Low carbon and mild steels have C contents of 0.05-0.15 wt.% and 0.16-0.29 wt.%, respectively. There are a large number of individual designations for carbon and mild steels defined by various standards organisations. Here, the general term carbon steel (C-steel) will be used to refer to all low carbon and mild steels and represents the alloys typically specified as container materials, unless otherwise stated.

The microstructural and mechanical properties of C-steel can be adjusted through thermal-mechanical treatments. Most heat treatments involve cooling the high-temperature austenite phase (γ Fe) at different rates to produce different amounts of ferrite (α Fe) and pearlite (a lamellar structure comprising ferrite and cementite, Fe₃C). Yield strengths can vary from ~300-700 MPa, with tensile strengths of 400-800 MPa.

The minor alloying elements can affect the corrosion behaviour and mechanical properties of C-steels (Lyon 2010). For example, Mn is added to improve the strength of the ferrite phase and Cu improves resistance to atmospheric corrosion. Other elements, in particular P and S, have an adverse effect on the mechanical and corrosion properties.
B2.3 Corrosion modes of carbon steel

B2.3.1 General corrosion

Figure B2.1 shows the potential-pH diagram for the Fe-H₂O system with Fe₂O₄, rather than Fe(OH)₂, as the Fe(II) stable solid phase. The formation of surface films is an important aspect of most forms of corrosion of C-steel, with dissolution under film-free conditions only occurring in acidic solutions. The nature of the film depends on the composition of the aqueous phase as well as the potential and pH, with ions such as Cl⁻, SO₄²⁻, and CO₃²⁻ often incorporated into the film. Whether the film is passive or merely protective depends on the film structure and is determined by kinetic, rather than thermodynamic, factors.

The general corrosion behaviour of C-steel under aerobic and anaerobic conditions is typically discussed separately, although the transition between these two phases can be important for localised corrosion, as discussed later. Honda et al. (1991) studied the aerobic corrosion of C-steel in compacted bentonite as a function of time, Cl⁻ concentration, bentonite density, and temperature. The corrosion rate was thought to be controlled by the rate of supply of O₂, although there was a minor effect of [Cl⁻], with the rate higher in sea water (~0.5 mol/L Cl⁻) than in distilled water. Corrosion rates after 90 d exposure were of the order of 10 μm/y.

A significant amount of work has been directed towards determining the rate of anaerobic corrosion of C-steel. This interest is two-fold; first, the lifetime of C-steel containers is largely determined by the rate of anaerobic corrosion and, second, the rate of anaerobic corrosion determines the rate of formation of H₂ and Fe(II), both of which can impact the properties of the surrounding barriers.

Figure B2.2 shows the measured time dependence of the anaerobic corrosion rate in a dilute granitic groundwater solution measured based on the rate of H₂ generation (Smart et al. 2001, 2002). The corrosion rate decreases with time due to the formation of a protective surface film, identified as Fe₃O₄. The apparent steady-state corrosion rate after ~6 months exposure was of the order of 0.1-1 μm/y. There is no apparent difference between the corrosion rates for C-steel and cast iron.
Figure B2.1: Potential-pH diagram for the Fe-H₂O system at 25°C with Fe₃O₄ as the stable Fe(II) solid phase (Pourbaix 1974).

Figure B2.2: Time dependence of the corrosion rate of cast iron and carbon steel in deaerated granitic groundwater measured using the rate of hydrogen generation (Smart et al. 2001, 2002).
In cement or in alkaline solutions simulating cement pore water, the steady-state corrosion rate of C-steel is <0.1 μm/y (Smart et al. 2004). Chloride ions were found to have little effect on the corrosion rate, but Ca ions were found to improve the protectiveness of the film. A ferrous hydroxide (Fe(OH)₂) film was formed at low temperatures (30°C), with Fe₃O₄ formed at higher temperatures (50°C and 80°C).

There are differences between the anaerobic corrosion behaviour of C-steel in bulk solution and in compacted bentonite (Figure B2.3). Many of these differences seem to result from the ability of the clay to adsorb or react with Fe(II). Corrosion rates are higher in compacted bentonite and take longer to achieve steady state as a result of a less-protective surface film. The film composition and structure are also different, with carbonate species incorporated into a “dense product layer” in bentonite compared with the compact Fe₃O₄ film formed in bulk solution (King 2008, Johnson and King 2008).

In the French programme, the horizontal tunnels for the disposal of HLW are not filled to allow for retrieval of the waste if necessary. As a consequence, the corrosion behaviour of steel in direct contact with the Callovo-Oxfordian clay is of interest (Martin et al. 2008, 2012).

An important aspect of the anaerobic corrosion of C-steel is the potential impact of corrosion products on other barriers in the multi-barrier disposal system. Anaerobic corrosion results in the formation of both H₂ and Fe(II).

<table>
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<tr>
<th>Corrosion rate and time dependence</th>
<th>Bulk solution</th>
<th>Compacted clay</th>
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<tr>
<td>~0.1 μm y⁻¹ steady-state after 4-6 months</td>
<td>~1 μm y⁻¹ still decreasing after 4 y</td>
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Corrosion products: composition and structure

- Duplex spinel-type/Fe₃O₄ structure
- Corrosion product layer containing FeCO₃/(Fe,Ca)CO₃ and adjoining altered soil layer

Figure B2.3: Comparison of the corrosion behaviour of carbon steel in bulk solution and in compacted bentonite (Johnson and King 2008).
Gas generation and transport has been addressed in some detail by Nagra in relation to a proposed GDF in Opalinus Clay. Figure B2.4 shows the predicted rate at which gas can be transported away from the container through Opalinus Clay (the "gas transport capacity") for various transport mechanisms as a function of gas pressure (Nagra 2004). The gas transport capacity can be converted to an equivalent anaerobic corrosion rate for C-steel, with a $H_2$ flux of $10^{-5}$ m$^3$(H$_2$ STP)·m$^{-2}$·y$^{-1}$ being equivalent to a corrosion rate of 0.002 μm/y (for Fe corrosion to Fe$_3$O$_4$). Thus, even for the low corrosion rates associated with the use of a cementitious buffer (of the order of 0.01 μm year$^{-1}$), dissolved $H_2$ would not be removed fast enough and a separate gas phase would form. For the corrosion rates observed in compacted bentonite, gas transport would be via two-phase flow, although some form of dilatancy-controlled transport might occur at higher pressures (the horizontal grey bar in Figure B2.4 represents a range of anaerobic corrosion rates of between 1 μm/y and 10 μm/y).

![Gas transport capacity diagram](image-url)

**Figure B2.4: Gas transport capacity for various gas transport mechanisms in Opalinus Clay as a function of the total pressure (Nagra 2004).**

For a disposal concept that does not include a buffer, the production of $H_2$ may have less impact on other barriers, although a significant $H_2$ partial pressure could build up in a GDF.

Ferrous ions produced by anaerobic corrosion will cause the alteration of bentonite in a disposal concept that includes a clay buffer (Carlson et al. 2006; Guillaume et al. 2003, 2004; Marcos 2003; Johnson et al. 2005; Lanson et al. 2012; Perronnet et al. 2008; Savage et al. 2010; Wersin and Snellman 2008; Wilson et al. 2006a,b; Wilson et al., 2011). The primary concern is that swelling smectite clays can be converted to Fe-rich non-swelling minerals, such as berthierine, cronstedite, and chlorite, which will have a lower swelling capacity than the smectite component of the bentonite. It is also possible that Fe-rich smectite (saponite) could form as an alteration product (Wilson et al., 2006a,b).
In addition, corrosion experiments carried out under the European NF-PRO project with iron wires embedded in compacted bentonite show that increased concentrations of iron in the bentonite affect some physical properties of the bentonite, with increased hydraulic conductivity, decreased swelling pressure, and decreased cation exchange capacity being exhibited by altered bentonite (Smart et al., 2006).

In addition to these deleterious effects, C-steel corrosion products may have beneficial effects on other barriers, in particular the wasteform. The formation of high-surface-area Fe(II)/Fe(III) corrosion products will provide adsorption sites for radionuclides released from the wasteform following container failure. However, the potential for radionuclide adsorption to container corrosion products is generally considered to be a ‘reserve FEP’ and may be excluded from safety assessments (e.g. Nagra, 2002).

Another potential benefit associated with container corrosion is that H₂ suppresses the dissolution rate of spent fuel (Shoesmith 2008).

**B2.3.2 Localised corrosion**

King (2007) identified three mechanisms by which C-steel containers might be susceptible to localised corrosion:

1. localised breakdown of a passive film leading to crevice corrosion or pitting;
2. non-uniform wetting of the surface due to deliquescence of surface contaminants, resulting in the spatial separation of anodic and cathodic sites; and
3. reductive dissolution of Fe(III) corrosion products during the transition from aerobic to anaerobic conditions.

Whether the container surface will be passive or not depends on the nature of the near-field environment and how it evolves over time. Passivity is more likely under aerobic conditions. In cementitious environments, the surface is likely to be passive due to the formation of a stable Fe₃O₄ film (Figure B2.1), possibly covered by a precipitated layer of “FeOOH” (either lepidocrocite or goethite). The Fe₃O₄ layer will persist under anaerobic conditions, possibly ensuring passivity until degradation of the cement barrier. However, localised breakdown of the film by, for example Cl⁻ ions is only likely under aerobic conditions because the corrosion potential is less than the threshold potentials for pitting and crevice corrosion under anaerobic conditions (Figure B2.5). It is interesting to note from Figure B2.5 that, unlike the situation for copper, increasing pH does not necessarily decrease the probability of localised corrosion as E_{CORR} shifts to more-positive potentials with increasing pH.

In disposal concepts that include a bentonite buffer, evidence from JNC (2000) suggests that C-steel is not passive in the moderately alkaline pore water. This is an important observation since it implies that localised corrosion of C-steel containers due to the breakdown of a passive film should not occur.

Regardless of the pH of the near-field environment, localised corrosion by Cl⁻ could be initiated if the surface wets non-uniformly during GDF resaturation. Deliquescence of water on salt crystals or other contaminants on the container surface will lead to the formation of macro and micro water droplets connected by a thin adsorbed water layer (Figure B2.6). The cathodic reduction of O₂ will occur on and around the micro-droplets and the periphery of the macro-droplet, since these regions experience the highest O₂ flux. The anodic reaction will be focussed in the centre of the macro-droplet where O₂ replenishment is limited. As for the first mechanism of localised attack, this spatial separation of anodic and cathodic processes will only operate during the aerobic phase.
The third localised corrosion mechanism is illustrated in Figure B2.7. During the aerobic-anaerobic transition, the reductive dissolution of Fe(III) corrosion products could become coupled to the dissolution of Fe at the base of pores in the underlying film. This form of electrochemical coupling occurs in a number of systems (e.g., Qin et al. 2004) and is responsible for the localised corrosion of C-steel steam generator shells during chemical cleaning to remove Fe$_3$O$_4$ deposits (Shoesmith et al. 1981).

It is evident from the discussion above that localised corrosion will be limited to the aerobic and aerobic-anaerobic transition periods. Localised corrosion will not occur under anaerobic conditions.

Various methods have been used to assess the extent of damage from the localised corrosion of C-steel. The most common approach is the pitting factor, the ratio of the maximum to the mean depth of corrosion (Féron et al. 2009, JNC 2000, Johnson and King 2008, Taniguchi et al. 2011). Extreme-value analysis of pit-depth data or the development of simple pit penetration expressions have also been used (Taniguchi et al. 2011).

![Figure B2.5: Dependence of repassivation potentials for the pitting and crevice corrosion and the corrosion potential of carbon steel on pH (Fukuda et al. 1995).](image-url)
Figure B2.6: Spatial separation of anodic and cathodic sites for the non-uniform wetting of a steel surface (after Zhang et al. 2005).

Figure B2.7: Illustration of possible spatial locations for anodic and cathodic reactions on a film-covered C-steel surface (King 2007).

B2.3.3 Environmentally assisted cracking

The two forms of environmentally assisted cracking of concern for C-steel containers are stress corrosion cracking (SCC) and hydrogen-induced cracking (HIC) (and, more generally, all forms of H-related degradation).

Stress corrosion cracking of C-steel is known to occur in a number of different environments, including: caustic, phosphate, and nitrate solutions; high-temperature water, CO₂/CO₂ mixtures, and HCO₃⁻/CO₃²⁻ (King 2010). Of these various environments, none are likely to form in a GDF except for HCO₃⁻/CO₃²⁻ in disposal concepts that include bentonite buffers and, possibly, caustic solutions in disposal concepts that include a cement buffer.

The SCC of pipeline steels in HCO₃⁻/CO₃²⁻ environments occurs in two forms, so-called high-pH SCC and near-neutral pH SCC (Parkins 2000). High-pH SCC occurs in concentrated solutions at pH 9.5-11.5 and is characterised by intergranular cracking resulting from a slip dissolution (film rupture) mechanism. The concentrated solution forms due to the action of the cathodic protection system used on pipelines or, alternatively, by evaporation of more-
Corrosion of Carbon Steel

dilute solutions. Cyclic loading is required to promote crack-tip film rupture. Near-neutral pH SCC occurs in dilute HCO₃⁻ solutions at pH 5.5-7.5 and cracking is transgranular in nature. Cyclic loading is a pre-requisite to produce crack growth via a corrosion fatigue mechanism, possibly involving hydrogen. Because of the important role of cyclic loading in both forms of cracking, it is unlikely that a statically loaded container would be susceptible to SCC in HCO₃⁻/CO₃²⁻, even if such environments were to form.

Caustic cracking is typically associated with steam boilers and other equipment operating at high temperature (>100°C) (King 2010). This form of cracking is not commonly associated with C-steel in cementitious environments, possibly because the pore-water environment is unsuitable for cracking or because reinforced concrete structures are not generally exposed to elevated temperatures. Evaporative concentration of alkaline salts on the container surface during the early hot, aerobic phase could, however, establish conditions suitable for caustic cracking.

Hydrogen-related damage of C-steel may take several forms (King 2009a, Turnbull 2009). The forms of most concern for C-steel containers are: hydrogen-induced cracking (HIC), in which H accumulates under a stress gradient leading to internal crack formation; and blister formation, as a result of H accumulation at internal voids, laminations, or inclusions.

The susceptibility to HIC and blister formation increases with the strength of the material and the shape and distribution of inclusions in the steel (Figure B2.8). The susceptibility of a given material can be determined by comparing the threshold diffusible H concentration for the given strength to that expected to be generated by the service conditions. The latter is commonly measured in H permeation experiments, from which the total H concentration (Cₜₜ) can be determined. The total absorbed H concentration includes both the diffusible H and the hydrogen trapped in various trap sites in the alloy. Figure B2.9 shows values Cₜₜ as a function of pH, [Cl⁻], and [HS⁻]. The value of Cₜₜ decreases with both increasing pH, suggesting lower susceptibility in cementitious buffer, and, possibly, increasing [Cl⁻], and increases with increasing [HS⁻]. For a low-carbon or mild steel with a yield strength of 500 MPa, the critical total H concentration is ~10 ppm (10 μg·g⁻¹) (Figure B2.8). Comparison with the values in Figure B2.9 indicates that a C-steel container would only be susceptible to HIC at high [HS⁻], and likely only at concentrations greater than those expected in GDF environments.
Figure B2.8: Schematic illustrating the zones of susceptibility of carbon steel to hydrogen-related degradation mechanisms based on the total absorbed hydrogen concentration and the material yield strength (JNC 2000).

Turnbull (2009) has pointed out that there is a potential for internal HIC to occur, i.e., the initiation and growth of cracks from the inside of the container. Because a H2 gas phase is expected to develop on the outside of the container during the long-term anaerobic phase and because the diffusion of H in ferrite is relatively fast, hydrogen will diffuse through the container wall and slowly fill the interior void volume. Eventually, the internal H2 pressure will equalize with that at the exterior of the container, perhaps of the order of 5-10 MPa depending upon the hydrostatic pressure and bentonite swelling pressure (if used). Any defect on the inner surface of the final closure weld might then act as an initiation site for HIC, although both Turnbull (2009) and King (2009) concluded the probability of HIC of C-steel containers was low given the likely choice of a low-strength grade.

Figure B2.8 is based on data for “dirty” grades of C-steel with relatively high S contents leading to a large number of MnS inclusions. Modern steels have S contents <0.003 wt.% and have micro-alloy additions of Ca to control the shape of remaining inclusions (Hay 2003; King 2007, 2009a). Other additions, such as Cu, Co, Ni, and Cr, serve either to reduce the rate of H2 evolution or to reduce the fraction of adsorbed H that enters the steel.
Figure B2.9: Effect of various environmental parameters on the total absorbed hydrogen concentration (King et al. 2005). 1 mol/m$^3$ absorbed H corresponds to 0.127 ppm by mass.
B2.3.4 Microbiologically influenced corrosion

Carbon steel is susceptible to MIC under both aerobic and anaerobic conditions (Little et al. 1991). The two species most often associated with the MIC of C-steel are sulphate-reducing bacteria (SRB) and acid-producing bacteria (APB), although a wide range of other species can also play a role. The most aggressive forms of MIC occur under biofilms, which provide the opportunity for the spatial separation of anodic and cathodic processes.

Given this inherent susceptibility to MIC, the extent of MIC for a C-steel container is determined by the location and duration of microbial activity in a GDF environment (King 2009b).

B2.3.5 Galvanic corrosion

Carbon steel is one of the more active common construction materials and is noble to only magnesium, zinc, and aluminium alloys. As a consequence, C-steel would corrode more rapidly in contact with other more-noble materials, such as copper, Ni- or Ti-based alloys, in a galvanic couple. Microstructural or composition variation in welds could also lead to local galvanic effects and accelerated corrosion of the weld metal, heat-affected zone or base metal (depending on which regions are anodic and cathodic).

B2.3.6 Anthropogenic analogues

As for copper, there are many examples of anthropogenic analogues for steel containers (IAEA 2005, Miller et al. 2006). The use of analogues is a central part of the Japanese (Yoshikawa et al. 2008, 2009) and, in particular, the French (Monnier et al. 2008; Neff et al. 2006, 2006; Saheb et al. 2008, 2010, 2011) programmes, in the latter being based equally on the use of laboratory-scale studies, modelling, and analogues (Féron et al. 2009). The analogue studies, in particular, are used to build confidence in long-term predictions. Figure B2.10 shows how the results from analogue studies spanning a period of 1800 years are used to justify long-term corrosion rates. A similar approach is being used in Japan (Figure B2.11). Crossland (2005) has compiled corrosion rates of steels from a number of studies in both soil and in bulk solution and reports a decrease in corrosion rate with time. Crossland was also able to distinguish aerobic from anaerobic environments (Figure B2.12).
Figure B2.10: Comparison of inferred corrosion rates from artefacts examined by the authors (open symbols) and from literature data (full symbols) (Neff et al. 2006).

Figure B2.11: Comparison of extrapolated experimental corrosion rates and rates determined from artefacts from the Yamato Ancient Tomb (after Yoshikawa et al. 2008).
Figure B2.12: Compilation of corrosion rates of iron and steel exposed to soils and natural waters (Crossland 2005).
B2.4 Effect of environmental parameters

B2.4.1 Effect of redox conditions

The evolution of redox conditions in a GDF will lead to a corresponding evolution in the corrosion behaviour of a C-steel container. During the initial aerobic phase, general and localised corrosion are possible, with general corrosion and H-related damage possible during the long-term anaerobic phase.

General corrosion under aerobic conditions is characterised by the formation of Fe(III) corrosion products (Figure B2.13)

\[ 4\text{Fe} + 2\text{H}_2\text{O} + 3\text{O}_2 \rightarrow 4''\text{FeOOH}'' \quad (B2-1) \]

where “FeOOH” represents goethite (α-FeOOH), lepidocrocite (γ-FeOOH), or, in the presence of Cl⁻, akagenite (β-FeOOH). Crystallisation of the initially formed amorphous ferrixyhydroxide may also occur, resulting in the formation of maghemite (γ-Fe₂O₃) or hematite (α-Fe₂O₃). In Cl⁻, SO₄²⁻, or CO₃²⁻ containing waters, various forms of green rust (ferric oxide/hydroxide incorporating anions from the solution) may also form (Refait and Génin 1993). Ferric species are most likely to form by the homogeneous oxidation of Fe(II) by O₂, since the E_{CORR} will not be sufficiently anodic to cause the direct dissolution of Fe(III).

As the initially trapped O₂ is consumed, Fe(III) corrosion products will be transformed to magnetite, either by reaction with dissolved Fe(II) (Figure B2.13)

\[ 2\text{FeOOH} + \text{Fe(II)} \rightarrow \text{Fe}_3\text{O}_4 + 2\text{H}^+ \quad (B2-2) \]

or by reductive dissolution coupled to C-steel dissolution (Figure B2.7)

\[ 2\text{FeOOH} + \text{Fe} + 2\text{H}_2\text{O} \rightarrow 3\text{Fe(OH)}_2 \rightarrow \text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O} + \text{H}_2 \quad (B2-3) \]

Under anaerobic conditions, C-steel will dissolve to form ferrous hydroxide (Figure B2.13)

\[ \text{Fe} + 2\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_2 + \text{H}_2 \quad (B2-4) \]

which may be converted to Fe₃O₄ via the Schikkor reaction

\[ 3\text{Fe(OH)}_2 \rightarrow \text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O} + \text{H}_2 \quad (B2-5) \]

This evolution of the general corrosion behaviour also influences the evolution of other corrosion processes. Breakdown of the initially formed “FeOOH” or Fe₃O₄ passive film may lead to localised corrosion, depending upon the stability of the film (which, in turn, depends on the pH and temperature) and the concentration of aggressive species, particularly Cl⁻. As discussed in more detail above, localised corrosion is also possible during the aerobic-anaerobic transition due to the coupling of Fe(III) reduction to C-steel dissolution (Equation B2-3).

Under anaerobic conditions, H₂ evolution occurs and with it the possibility of H pickup and related H-degradation mechanisms. Localised corrosion ceases to be an issue because E_{CORR} is more-negative than the film breakdown potential.
B2.4.2 Effect of chloride

The most important effect of Cl\(^{-}\) is the influence on the possibility of film breakdown and localised corrosion during the aerobic phase. Blackwood et al. (2002) studied the effect of Cl\(^{-}\) concentration on the pitting of C-steel in Nirex Reference Vault Backfill (NRVB) as a function of temperature. In alkaline solution, the critical pitting temperature (CPT) decreased with increasing [Cl\(^{-}\)], from <70\(^{\circ}\)C at 440 mg/L Cl\(^{-}\) to <20\(^{\circ}\)C at 1000 mg/L Cl\(^{-}\). Expressed alternatively, in terms of a critical Cl\(^{-}\) concentration [Cl\(^{-}\)]\(_{CRIT}\), [Cl\(^{-}\)]\(_{CRIT}\) varies from >6,000 mg/L Cl\(^{-}\) at room temperature to <400 mg/L at 50\(^{\circ}\)C and 80\(^{\circ}\)C. These experiments were conducted in nominally aerated conditions, so the values of CPT and [Cl\(^{-}\)]\(_{CRIT}\) represent those conditions under which E\(_{CORR}\) exceeds the pitting potential (E\(_{PIT}\)).

In near-neutral pH conditions in bentonite pore water, the data in Figure B2.5 indicate that the C-steel surface is not passive, so that localised corrosion should not occur.

Chloride does not have a large effect on the rate of general corrosion. In aerated compacted bentonite, the rate of corrosion of C-steel at a [Cl\(^{-}\)] of a few tenths molar is higher than in distilled water, but does not increase within increasing concentration. Under anaerobic conditions, no significant differences have been reported in the corrosion rate for various synthetic groundwater solutions, with Kreis and Simpson (1992), for example, reporting no difference in the rate of H\(_2\) evolution in distilled water, Böttstein water 228 mg/L Cl\(^{-}\), and a solution containing 8000 mg/L Cl\(^{-}\).

B2.4.3 Effect of temperature

Temperature increases the probability of localised corrosion of C-steel due to film breakdown in cementitious environments (Blackwood et al. 2002). In moderately saline groundwaters ([Cl\(^{-}\]) > 1000 mg/L), the CPT is likely to be lower than the service temperature.
for SF and, possibly, for HLW. Although pits are likely to initiate, it does not necessarily mean that they will propagate through the wall to cause container failure, since the pits tend to spread out as they grow deeper (Kursten et al. 2004).

There is no evidence that C-steel becomes passive in bentonite at elevated temperature. Honda et al. (1991) report a modest temperature dependence for the rate of general corrosion in aerated bentonite. The reported activation energy of 1 kJ/mol to 4 kJ/mol is less than that which would be expected for a diffusion- (~15 kJ/mol) or activation-controlled (~60 kJ/mol) corrosion reaction, and presumably indicates joint rate-control by a number of individual processes with different temperature dependences.

Under anaerobic conditions, increasing temperature appears to promote the formation of a more-protective surface film. Both Schenk (1988) and Smart et al. (2001, 2002) observed more-adherent and protective films at temperatures >50°C, although there is no obvious effect on the time-averaged (weight-loss) corrosion rates. The apparent improved protectiveness at higher temperatures may be due to the temperature dependence of the Schikkor reaction (Equation B2-5), which is kinetically slow at temperatures <80°C (Smart et al. 2001, 2002).

There may be an increased risk of various forms of SCC with increasing temperature (King 2010), both because suitable environments are more likely to form at elevated temperature and also because of faster crack growth rates.

**B2.4.4 Effect of pH**

Increasing pH promotes the passivation of C-steel (Kursten and Druyts 2008, Kursten et al. 2011, Macdonald et al. 2011, Saleh et al. 2011). The effect of passivity is most evident from the rates of anaerobic general corrosion, which are of the order of 1 μm/y at near-neutral pH and <0.1 μm/r in alkaline solution. Along with this passivity, however, comes a higher probability of the initiation of localised corrosion, as discussed above.

Increasing pH is likely to result in a lower probability of environmentally assisted cracking. There is no indication that either caustic cracking or high-pH SCC occurs in cementitious environments, the former possibly because of generally ambient service temperatures for reinforced concrete structures and the latter because concentrated CO$_3^{2-}$/HCO$_3^-$ solutions do not form in cement pore water because of the limited solubility of CaCO$_3$. Furthermore, the sub-surface hydrogen concentration decreases with increasing pH (Figure B2.9(a)), resulting in a lower probability of H-related damage.

**B2.4.5 Effect of sulphur species**

Sulphide (HS$^-$) and thiosulphate (S$_2$O$_3^{2-}$) ions are produced by the dissolution of pyrite. Sulphide ions affect both the general corrosion behaviour of C-steel and the rate of H pick up. Unlike the adverse effect of thiosulphate ions on the localised corrosion of stainless steels, evidence from the Belgian programme (Kursten et al. 2004) suggests no similar detrimental effect for C-steel.

Sulphide ions affect the rate of general corrosion and the fraction of hydrogen absorbed by the material. The rate of general corrosion is affected by the nature of the film that is formed and the potential for an increase in the cathode surface area. General corrosion will result in the formation of an “iron sulphide” film

\[
\text{Fe} + \text{HS}^- \rightarrow \text{Fe}_{1+x} \text{S} \quad \text{(B2-6)}
\]
where the corrosion product first formed is typically mackinawite (ASM 1987, 2005). The formation and transformation of sulphide films on C-steel are complex and many possible solid species are possible. The degree of protection offered by the “iron sulphide” depends on the concentration or, more correctly, the flux of HS\(^-\) to the corroding surface. The non-stoichiometric nature of iron sulphide films raises the possibility that they could act as cathodes for the reduction of oxidants.

The other major effect of HS\(^-\) on the corrosion behaviour of C-steel is the increase in the absorbed hydrogen concentration (Figure B2.9(c)) and the possibility of H-related damage (Figure B2.8). Sulphide acts as a H-atom recombination poison, effectively increasing the surface concentration of adsorbed H atoms and, hence, also leading to an increase in the absorbed hydrogen concentration. However, significant interfacial [HS\(^-\)] would be required to increase the susceptibility to the point at which H-related damage might be a concern, even for the older steels with high MnS inclusion contents to which the data in Figure B2.8 refer.

**B2.4.6 Effect of other anions and cations**

Carbonate ions cause the passivation of C-steel through the formation of precipitated FeCO\(_3\) (JNC 2000). However, since the generic UK groundwaters have low HCO\(_3\)/CO\(_2\)\(^-\) contents (King and Watson 2010), the only source of carbonate species would be the dissolution of carbonate minerals in the bentonite clay or host rock. In bentonite clay, JNC (2000) found that C-steel is active and that the carbonate content of the pore water is insufficient to promote passivation.

Other common groundwater species have no or minimal effects on the corrosion behaviour of C-steel.

**B2.4.7 Effect of gamma radiation**

Gamma irradiation leads to an increase in corrosion rate above a threshold absorbed dose rate, the value of which depends on the environment (Shoesmith and King 1999). In synthetic seawater, the threshold dose rate is ~3 Gy/h, but there is a minimal effect even at a dose rate of 300 Gy/h in lower salinity groundwaters (Smart et al. 2008). In alkaline solution, a dose rate of 25 Gy/h had a negligible impact on the rate of H\(_2\) generation from the anaerobic corrosion of C-steel at 25 and 80°C in dilute Cl\(^-\) solutions (Winsley et al. 2011). In aggressive Mg-containing brines, moderate dose rates (0.1-10 Gy/h) cause the formation of more-protective corrosion products resulting in a decrease in corrosion rate, but higher dose rates (1000 Gy/h) can cause significant increases in corrosion rate (Kursten et al. 2004).

For reference, the maximum absorbed dose rate for the standardised HLW/spent fuel conceptual container design is <1 Gy/h (NDA 2013).

**B2.4.8 Effect of unsaturated conditions and atmospheric exposure**

The evolution of the GDF environment and the development of conditions for atmospheric corrosion and corrosion in unsaturated buffer materials are described in the main text. Aqueous corrosion processes are possible once an electrolyte forms on the surface in response to the increasing relative humidity in a GDF (either by the deliquescence of salt contaminants, capillary condensation in pores, and/or physisorption of H\(_2\)O). Prior to this stage, only dry-air oxidation is possible.
Carbon steel is also suitable for use as a container material in disposal concepts that do not include a buffer. The kinetics of dry-air oxidation and film growth have been studied in some detail in the French programme (Desgranges et al. 2004). In common with other engineering materials, C-steel will be subject to aqueous corrosion processes in thin adsorbed water films if the RH in the GDF exceeds 60-70%.
B2.5 Effect of the operational period

King et al. (2011) have considered the effects of various operational factors on the corrosion behaviour of HLW/SF container materials during the pre-closure period, as well as the consequences for the post-closure phase. Various factors associated with container fabrication, interim storage and handling, and the period post-emplacement but prior to final sealing of the GDF were considered. For the current purposes, these factors can be summarised as follows:

- Mechanical damage – as might occur due to mis-handling or accidents during the operational phase.
- Cross-contamination/dissimilar metal corrosion – resulting, for example, from the smearing of Fe on the container surface from the use of steel-based tools or poorly designed container identification markers.
- Internal corrosion – due to inadequate drying of defected SF, and influenced by the temperature and burn-up of the fuel.
- Corrosion during interim storage – as impacted by the location and environmental control of the store (and the effect on temperature, relative humidity, and the degree of surface contamination), the stacking of containers, and the possible use of shielding casks.
- Undetected and/or un-repaired surface defects.
- Extended operational phase following container emplacement and prior to closure of the GDF – potentially resulting in additional access of O₂ and/or delayed resaturation of the buffer material(s).
- Poor quality control over emplacement operations – resulting, for example, in missing or non-optimal buffer material(s).

Further details of all of the individual factors considered can be found in King et al. (2011).

Of these various factors, those of most concern (‘critical’ condition) are the possibility of an extended period following emplacement of the C-steel containers but prior to complete sealing of the GDF and poor quality control over the emplacement of the buffer material (King et al. 2011). During such a period, atmospheric O₂ may diffuse (or be advectively transported in unsaturated buffer and backfill materials) from the open access ways and tunnels to the emplaced containers. Additional general corrosion would occur and, perhaps of more concern, localised attack is possible, especially if the surface is non-uniformly wetted in an unsaturated disposal room or tunnel.

Missing or sub-standard buffer material could also adversely affect the corrosion behaviour of a C-steel container during the post-closure period. For example, if the pH of a cementitious buffer was not sufficiently high, localised corrosion could occur during the post-closure aerobic period. Microbial activity is also more likely in low-pH cement pore waters, as it is for bentonite with a dry density less than 1.6 Mg.m⁻³ (King 2009b). The occurrence of microbial activity on the container surface would represent a ‘critical’ condition.

Differences in the bentonite density (e.g., as a result of operational errors as inherent in the GDF design) and/or differences in the spatial distribution of bentonite swelling could lead to differential aeration cells. It has been suggested that such effects could lead to ‘focussed’ or localised corrosion, although there are no data to support such a suggestion (Landolt et al. 2009).
Operational factors of less concern (‘marginal’ conditions), but still requiring consideration of the impact on the corrosion behaviour of the container, include (King et al. 2011):

- Mechanical damage during handling and emplacement – C-steel is susceptible to strain hardening (also referred to as work hardening or cold working) in which plastic deformation results in an increase in strength and loss of ductility of the affected metal. This, in itself, is not an issue for the integrity of the containers but may be of concern if the container is subsequently exposed to an environment in which environmentally assisted cracking might occur. For example, the susceptibility to HIC is higher for higher strength materials (Figure B2.8).

- Internal corrosion resulting from entrained water in defected SF – Burt et al. (2013) have considered the case of a C-steel SF container with the maximum conceivable amount of entrained water (1400 g) and the consequences for over-pressurisation and internal corrosion during interim storage and disposal in the GDF. There is no significant loss of integrity of the container as a result of either over-pressurisation or corrosion.

- Corrosion during interim storage – if the temperature, relative humidity, and the ingress of corrosive contaminants in the store environment are not properly controlled, atmospheric corrosion of the container will occur. The extent of corrosion will depend on the nature of the store environment and the length of storage. Localised atmospheric corrosion could occur, especially if the surface is non-uniformly wetted.

- Undetected/un-repaired defects – Sanderson et al. (2013) have assessed the impact of various internal and external defects on the integrity of a C-steel SF container during interim storage and disposal in the GDF. The defects act as stress intensifiers and may be subject to HIC at sufficiently high absorbed hydrogen concentrations. Sanderson et al. (2013) concluded that internal defects were of more concern, as those on the outside of the container are removed by external corrosion during the post-closure period. However, for the set of conditions considered in the analysis, container failure is more likely to result from plastic collapse following wall loss from general corrosion than by HIC.
B2.6 Lifetime predictions

Lifetime predictions for C-steel containers are generally based on estimates arising from a combination of general corrosion and localised attack (Johnson and King 2003, JNC 2000, King 2007, Marsh and Taylor 1988). Typically, the extent of general corrosion is estimated based on mass-balance arguments for the aerobic phase (based, for example, on the stoichiometry shown in Equation B2-1), and empirical corrosion rates for anaerobic corrosion. The amount of aerobic corrosion depends on the GDF design and is generally of the order of <1 mm (JNC 2000, Johnson and King 2003, Marsh and Taylor 1988). The anaerobic corrosion rate that has been used ranges from 0.1-10 μm/y, with a value of 1-3 μm/y generally considered appropriate for C-steel in compacted bentonite.

Electrochemical models have also been used to assess the extent of aerobic and anaerobic corrosion of C-steel (JNC 2000, Marsh and Taylor 1988), but are inevitably conservative since they do not take into account the substantial reduction in corrosion rate as a result of the formation of a protective surface film. King and Kolar (2012) have developed a reactive-transport model that does account for the formation of a protective Fe₃O₄ film. The corrosion rate is predicted to decrease with time, attaining a steady state, the value of which depends on the porosity of the corrosion product film. The model also predicts the impact of gas generation and the alteration of bentonite by dissolved Fe(II).

Marsh and co-workers (Marsh and Taylor 1988, Marsh et al. 1989) included radiolysis effects in their electrochemical and empirical corrosion models through the use of an effective G-value (the yield of oxidising radiolysis products per 100 eV of absorbed energy) based on the observed effect of γ-radiation at doses rates >1 Gy/h.

Localised corrosion, in the form of pitting, has been assessed based on empirical data rather than mechanistic pitting models. Marsh and co-workers developed a time-dependent expression for the maximum penetration (P) based on extreme-value statistical analysis of laboratory data

\[ P = 8.35t^{0.46} \quad \text{(B2-7)} \]

where t is the time in years (Marsh and Taylor 1988; Marsh et al. 1987, 1989). This expression was variously applied: (i) for the entire disposal period (Marsh and Taylor 1988) or (ii) for the period of passivity, deemed to correspond to the period for which the O₂ flux exceeded the passive current density (Marsh et al. 1987). JNC (2000) also assumed that the C-steel surface would not be passive in compacted bentonite based on experimental evidence. Others have used an empirical pitting factor based on data from laboratory studies and long-term burial trials (JNC 2000). Johnson and King (2003) used a conservative pitting factor of 10 for the aerobic phase only, whereas JNC (2000) applied a pitting allowance for both the aerobic and anaerobic periods, even though localised corrosion would not be expected in the absence of O₂.

In addition to allowances for general and localised corrosion, various allowances have also been made for MIC. In all cases, the only form of MIC considered is that due to sulphate-reducing bacteria (SRB), and then only to the extent that additional general corrosion results from the formation of sulphide. Marsh and Taylor (1988) estimated the maximum amount of corrosion due to SRB based on the assumption that organic carbon would limit the extent of sulphate reduction, resulting in an additional 13 mm of wall loss. In one of the two lifetime assessments published by JNC (2000), it was conservatively assumed that all of the sulphate in the bentonite-based sealing material would be converted to sulphide, leading to an additional 0.5 mm of general corrosion. In the second lifetime assessment in JNC (2000), it was assumed, based on experimental evidence, that there would be no microbial activity in the compacted bentonite surrounding the container and, hence, no additional corrosion.
allowance was made. A similar approach was taken by Johnson and King (2003) and King (2007) in the Swiss and Canadian programmes, respectively, based not only on the earlier Japanese experience but also based on the results from the extensive experimental programme on the viability of microbes in compacted bentonite carried out in Canada and Sweden (King 2009b, Masurat et al. 2007, Stroes-Gascoyne et al. 2007).

Various arguments have been made to support the position that environmentally assisted cracking will not occur. Hydrogen-related failures are thought to be unlikely either because (a) the sub-surface hydrogen concentration is less than the threshold value for various forms of damage (Johnson and King 2003, JNC 2000, King 2009a, Turnbull 2009) or (b) the susceptibility of the heat-affected zone of the final closure weld can be avoided by suitable post-weld heat treatment (Marsh et al. 1987). Stress corrosion cracking has been judged to be unlikely because of (a) the use of pre- and post-weld stress relief (Marsh and Taylor 1988, Marsh et al. 1987) of (b) the absence of cyclic loading and the necessary SCC environments (Johnson and King 2003, King 2010).

The corrosion assessments summarised above have been used more to predict the extent of corrosion within a given period of time (typically 1000 years), than to predict the lifetimes of specific container designs. The predicted depths of corrosion range from 12 mm after 1000 years (Johnson and King 2003) to as much as 230 mm for the same time period (Marsh and Taylor 1988). There has been a tendency for damage predictions to become less conservative in recent years as additional research has reduced some of the earlier uncertainty. For example, there are now a larger number of reliable measurements of the anaerobic corrosion rate in compacted bentonite and bulk solution, as well as consensus that microbial activity is not possible in compacted bentonite (at a dry bentonite density of approximately 1.6 g/cm³ or higher). In addition, it is now recognised that discrete pits are unlikely to be sustained and that the surface will take on a roughened appearance over time rather than be deeply pitted.
B2.7 ‘Critical’ and ‘marginal’ conditions

Table B2.1 lists various environmental parameters and the value beyond which the use of C-steel as a container material would either result in unacceptable performance (‘critical’ condition) or which would require an in-depth assessment to ascertain whether the required performance could be obtained (‘marginal’ condition).

A number of issues go into the decision of whether any factor or the value of a given parameter represents a ‘critical’ or ‘marginal’ condition. In addition to the impact of the factor or parameter on the corrosion behaviour of the container, the consequences of the container design and the target lifetime must also be taken into consideration. For example, a given parameter might be marginal for a thick-walled container design (or if only a relatively short container lifetime is required), but critical if the corrosion allowance is smaller (or if a long container lifetime is needed). To the extent possible, these other considerations are taken into account here in deciding whether a factor or parameter is critical or marginal.

The environmental and service conditions that are most critical for a C-steel container are:

- Microbial activity on the container surface should be avoided, since relatively rapid and localised attack is possible under biofilms.
- Carbon steel is unsuitable for use in a permanently aerobic environment because of high rates of general corrosion and the possibility of localised attack.

Other, marginal, conditions are described in Table B2.1.

Table B2.2 summarises the impact of operational factors on the integrity of a C-steel container. The two critical conditions are deemed to be:

- An extended operational phase allowing ingress of atmospheric O₂, resulting in general corrosion and possible localised attack.
- Sub-standard backfill, specifically in the form of low density bentonite or low-pH cementitious backfill, both of which could permit near-field microbial activity and biofilm formation on the container surface. Differences in bentonite density or swelling could lead to differential aeration and possible localised corrosion (Landolt et al. 2009).

Other, marginal, conditions related to operational aspects are also described in Table B2.2.
Table B2.1: Summary of ‘critical’ (in bold font) and ‘marginal’ (in normal font) conditions for carbon steel HLW/SF containers under post-closure conditions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Critical/marginal condition</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Host rock</td>
<td>High sulphide mineral content (M)</td>
<td>A high sulphide mineral content in the host rock may be acceptable, but additional analyses would be required to determine the flux of HS⁻ to the container. In addition, the impact on hydrogen-related damage mechanisms would need to be assessed.</td>
</tr>
<tr>
<td>Redox conditions</td>
<td>Permanently aerobic (C)</td>
<td>C-steel is unsuitable for use in aerobic environments because of the high rate of general corrosion and the possibility of localised corrosion.</td>
</tr>
<tr>
<td>Temperature</td>
<td>&gt;200°C (M)</td>
<td>The use of C-steel at elevated temperatures in backfilled systems is unlikely to be limited by any corrosion consideration but by the temperature limit for the bentonite or cementitious buffer. C-steel is also suitable for use at elevated temperature without a buffer.</td>
</tr>
<tr>
<td>Gamma radiation</td>
<td>&gt;10 Gy/hr (M)</td>
<td>The threshold for a detrimental effect of γ-radiation has not been established but is likely to be &gt;10 Gy/hr.</td>
</tr>
<tr>
<td>Buffer material and near-field mass transport</td>
<td>None</td>
<td>The use of C-steel is appropriate for bentonite or cementitious buffers and for un-backfilled GDF. However, because of the increased susceptibility to localised corrosion by Cl⁻ at high pH, the use of cementitious buffer in host media with saline groundwater should be carefully reviewed.</td>
</tr>
<tr>
<td>Chloride concentration</td>
<td>&lt;400 ppm with cement buffer (M)</td>
<td>The [Cl⁻] required for localised corrosion in cementitious buffer is &lt;400 ppm at 50°C based on measurements of the critical pitting potential in NRVB (Blackwood et al. 2002). The use of C-steel with a cement buffer at higher [Cl⁻] is still possible, but will require a more-detailed analysis of the possibility of localised corrosion.</td>
</tr>
<tr>
<td>Other groundwater species</td>
<td>&gt;6000 mg/L bicarbonate (M)</td>
<td>There are no other groundwater anions or cations that represent a specific issue for C-steel. The presence of high bicarbonate concentrations (&gt;0.1 mol/L, 6000 ppm) could induce passivation of C-steel and increase the probability of localised corrosion.</td>
</tr>
<tr>
<td>Sulphur species</td>
<td>Uncertain</td>
<td>Sulphide will cause accelerated general corrosion and increased susceptibility to hydrogen-related damage. However, the typical groundwater concentrations likely to induce susceptibility to hydrogen damage are uncertain since much of the HS⁻ diffusing through a bentonite buffer will precipitate as iron sulphide before reaching the container surface. A</td>
</tr>
<tr>
<td>Parameter</td>
<td>Critical/marginal condition</td>
<td>Comment</td>
</tr>
<tr>
<td>--------------------------------------</td>
<td>----------------------------</td>
<td>-----------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Microbial activity</td>
<td>Microbial activity on the container surface (C)</td>
<td>Since C-steel is known to be susceptible to MIC under a biofilm and since no adequate model currently exists for predicting this form of corrosion, C-steel containers should not be used in environments in which there is a possibility of biofilm formation. In the current context, C-steel should not be used in an unbackfilled GDF unless it can be shown that there is no possibility of surface inoculation and microbial growth.</td>
</tr>
<tr>
<td>Residual stress and external load</td>
<td>None</td>
<td>It is accepted that there may be sufficient tensile strain on the container surface to support SCC in the unlikely event that a suitable environment is present. However, post-weld stress relief should be performed to reduce the probability of crack initiation. It is assumed that buckling collapse or creep failure is precluded through appropriate container design.</td>
</tr>
<tr>
<td>GDF saturation time</td>
<td>None</td>
<td>Provided no additional O₂ over and above that trapped initially enters the GDF during the unsaturated period, there is no deleterious effect of an extended saturation time on the corrosion behaviour of a carbon steel container.</td>
</tr>
</tbody>
</table>

Similar mechanism may occur for a cementitious buffer.
Table B2.2: Summary of ‘critical’ (in bold font) and ‘marginal’ (in normal font) conditions for carbon steel HLW/SF containers as a result of operational factors.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Critical/marginal condition</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical damage</td>
<td>Strain hardened material (M)</td>
<td>C-steel is susceptible to strain hardening which can result in an increase in strength and loss of ductility of the cold worked material. In turn, the hardened microstructure is generally more susceptible to environmentally assisted cracking in the presence of the appropriate environment(s).</td>
</tr>
<tr>
<td>Cross-contamination/dissimilar metals*</td>
<td>None</td>
<td>Since the handling equipment is likely to be fabricated from steel, contamination from this source is not of concern. Carbon steel is amenable to autogenous welding methods (i.e., without the need for a filler material), and is less likely to be impacted by an error in the composition of the filler alloy than other candidate container materials.</td>
</tr>
<tr>
<td>Internal corrosion</td>
<td>Entrainment of water in damaged SF (M)</td>
<td>For credible amounts of entrained water, there is unlikely to be significant damage to a C-steel container from over-pressurisation or corrosion. However, the H₂ produced by internal corrosion will contribute to long-term H absorption and possible HIC. The extent of internal pressurisation (due to H₂ formed from internal corrosion of ferrous materials and/or radiolysis, or due to He produced from radioactive decay) is dependent on the container design, especially the internal void volume. Internal pressurisation is not considered to be a critical condition and can be managed through ensuring adequate drying of spent fuel and/or sufficient internal free volume.</td>
</tr>
<tr>
<td>Corrosion during interim storage</td>
<td>Poor control over environmental conditions (M)</td>
<td>A period of extended interim storage during which the temperature, relative humidity (RH), and/or level of contamination in the store are poorly controlled could lead to atmospheric corrosion with possible localisation.</td>
</tr>
<tr>
<td>Undetected/unrepaired surface defects</td>
<td>Internal and external crack-like defects (M)</td>
<td>Internal and external crack-like defects will increase the possibility of HIC. An assessment of the likelihood of cracking is required for credible defect sizes, stresses, and absorbed H concentrations.</td>
</tr>
<tr>
<td>Parameter</td>
<td>Critical/marginal condition</td>
<td>Comment</td>
</tr>
<tr>
<td>------------------------------------------------</td>
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</tr>
<tr>
<td>Extended operational phase post-emplacement</td>
<td><strong>Ingress of</strong> atmospheric O₂ (C)</td>
<td>An extended period of O₂ ingress prior to sealing the disposal tunnel would lead to additional general and localised corrosion of a C-steel container. The threat increases with the duration of the operational phase.</td>
</tr>
<tr>
<td>Poor QA during emplacement</td>
<td><strong>Low density bentonite or low-pH cementitious backfill (C).</strong></td>
<td>Low density bentonite (&lt;1.6 Mg/m³) or low-pH cementitious backfill would allow near-field microbial activity and the possibility of biofilm formation on the container surface. Depending on the Cl⁻ concentration, a sub-standard cementitious backfill with low pore-water pH could also lead to an increased probability of localised corrosion during the aerobic phase in the GDF. Differences in the bentonite compaction density or swelling could set up differential aeration cells leading to localised corrosion.</td>
</tr>
</tbody>
</table>

* In common with all container materials, the use of a dissimilar metal for the lid (as might occur if different container materials were used for different waste types in the GDF) would be considered a critical condition.
B2.8 Advantages and disadvantages of carbon steel as a container material

Carbon steel has a number of advantages as a container material for the disposal of HLW/SF, including:

- Broad international experience and acceptance of C-steel as a suitable container material.
- Corrosion is typically uniform in nature, with minimal localised attack or SCC in saline environments.
- Adequate corrosion behaviour for a wide range of environmental conditions.
- Good mechanical properties and extensive experience in fabrication and sealing of large diameter structures manufactured from C-steel.
- Relatively simple lifetime prediction methodology.
- The existence of archaeological artefacts to support long-term predictions.

The disadvantages of C-steel as a container material include:

- Potentially adverse effects on other barriers, in particular the alteration of bentonite mineralogy and physical properties due to reactions with Fe(II) released during corrosion and the transport of gas through low-permeability sealing materials or host media.
- The perception that C-steel is suitable for relatively short-term containment (of the order of 1000 years) but not longer, despite evidence in support of lifetimes up to at least 10,000 years. As a consequence, C-steel may not be suitable for compensating for deficiencies in other barriers in the system.
B2.9 References


Corrosion of Carbon Steel

Quintessa Report for the UK Nuclear Decommissioning Authority, QRS-1525A-R1


